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Applying the silver-tube introduction method for thermal conversion elemental analyses and a new δ^2H value for NBS 22 oil†

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The $\delta^2H_{VSMOW-SLAP}$ value of total hydrogen of the international measurement standard NBS 22 oil was determined by a new method of sealing water in silver tubes for use in a thermal conversion elemental analysis (TC/EA) reduction unit. The isotopic fractionation of water due to evaporation is virtually non-existent in this silver-tube method. A new value for the $\delta^2H_{VSMOW-SLAP}$ of NBS 22 oil, calibrated with isotopic reference waters, was determined to be -116.9 ± 0.8‰ (1σ and n = 31). Published in 2010 by John Wiley & Sons, Ltd.

Solids analyzed for hydrogen isotopic composition should be normalized to the VSMOW–SLAP isotope scale.[1] These measurements commonly are performed by continuous-flow high-temperature conversion (HTC) techniques,[2–5] in which calibrated reference samples are interspersed among unknowns so that unknowns and known samples are treated identically.[6] The isotopic reference samples can be liquids sealed quantitatively in silver capsules[7] or calibrated solids. Ultimately, calibration of hydrogen-bearing liquids and solids must be made with isotopic reference waters to enable one to normalize to the VSMOW–SLAP scale. These waters commonly are sealed in silver capsules quickly by a method that minimizes evaporation of the small (0.2 to 1 μL) volumes.[8,9] Knöller *et al.* [10] used a strategy to minimize the effects of evaporation during weighing by weighing water under an argon atmosphere and loading an amount of water into capsules about 2 to 10 times larger (2 μL) than that commonly used. Recently, a semi-automated technique was described that enables one to seal water or other liquids, including oil, in a silver tube that can then be loaded into a TC/EA unit (Thermal Conversion/Elemental Analysis).[11] Because many aliquots with the same amount of water or oil can be prepared easily and quickly with this technique, we use it to calibrate liquid hydrogen isotopic reference materials. Details about the robustness of this method have been provided by Qi *et al.*[11]

The international isotopic measurement standard NBS 22 oil was prepared by S. Silverman (University of California, San Diego, California, USA), and it has found substantial use in the scientific community.[12] This material is intended for the stable isotopic calibration of hydrogen- and carbon-containing materials. Measurements of the δ^2H of NBS 22 were reported by Hut in 1987, and they ranged from -115.2 to -120.4‰.[12] No detailed information was provided about analytical methods used to obtain these values.[12] Therefore, NBS 22 is a good candidate for re-evaluation of its hydrogen isotopic composition.

In this paper, three strategies are used to calibrate NBS 22 oil. These include calibrating with (1) two calibrated reference waters with δ^2H values substantially different in isotopic composition from that of NBS 22 oil (-62.3 and -399.5‰); (2) two calibrated reference waters with δ^2H values close to that of NBS 22 oil (-62.3 and -150.7‰); and (3) one calibrated reference water with a δ^2H value as close to that of NBS 22 as possible. The last is a so-called point-to-point calibration method, and it eliminates the need for between-sample memory correction and mass spectrometric scale correction. In this paper, we present the values obtained from these three strategies and recommend a new δ^2H value for NBS 22 oil.

EXPERIMENTAL

In the Reston Stable Isotope Laboratory (RSIL)[13] of the U.S. Geological Survey (USGS), measurement of accurate δ^2H of waters is a critical endeavor for the USGS programs. The quantity δ^2H is defined by the relationship:

$$\delta^2H_{VSMOW} = \frac{R\,(^2H/^1H)_P - R\,(^2H/^1H)_{VSMOW}}{R\,(^2H/^1H)_{VSMOW}} = \frac{\dfrac{N\,(^2H)_P}{N\,(^1H)_P} - \dfrac{N\,(^2H)_{VSMOW}}{N\,(^1H)_{VSMOW}}}{\dfrac{N\,(^2H)_{VSMOW}}{N\,(^1H)_{VSMOW}}}$$

where $N(^2H)_P$ and $N(^1H)_P$ are the numbers of the two isotopes ^{2}H and ^{1}H of hydrogen in specimen P, $R(^2H/^1H)_P$ is $N(^2H)_P/N(^1H)_P$ in specimen P, and equivalent parameters

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follow for the international measurement standard VSMOW (Vienna Standard Mean Ocean Water). To be consistent with the Système International d'Unités, the SI (known in English as the International System of Units), which is published by the Bureau International des Poids et Mesures (BIPM), the extraneous numerical factor of 1000 should not appear in this equation in order that this equation should be written as a quantity equation and not as a numeric value equation.[14]

Reference waters were calibrated at the RSIL with a 60-port Pt-equilibration system connected to a VG Micromass model 602 dual-inlet isotope-ratio mass spectrometer (Waters/Micromass, Manchester, UK).[15–17] Gaseous hydrogen is equilibrated with water at 27.01 ± 0.03°C for a minimum of 2 h prior to mass spectrometric analysis. Isotopic results are logged to a Microsoft Access database in real time. A Microsoft Access-based program, LIMS (Laboratory Information Management Program) for Light Stable Isotopes,[18] is utilized to normalize[19] isotopic results to the VSMOW–SLAP isotope scale so that the δ^2H of SLAP (Standard Light Antarctic Precipitation) is −428‰ relative to VSMOW (Vienna Standard Mean Ocean Water).[1,20,21]

For introduction into the TC/EA unit, about 200 μg of reference water was sealed in each silver tube.[11] The silver-tube method is analogous to the method of using copper tubing for sealing of vacuum systems or for sealing noble gas samples, which is to pinch, seal, and cut to make a cold weld.[22] Silver tubing (#AG007050; Goodfellow, Oakdale, PA, USA) with a 99.95% purity and approximate dimensions of 0.7-mm o.d., 0.3-mm i.d., and 0.2-mm wall thickness can be used to seal water with this method. A semi-automated apparatus was used to produce tubes that were nearly identical in length, thus having the same amount of hydrogen.[11] We analyzed NBS 22 oil both in silver tubes and in silver capsules (3.5 × 5 mm, part # 041066; Costech, Valencia, CA, USA). A 5-cm length of silicone tubing (Cole-Parmer MasterFlex Platium L/S 13, part # 96410-13; Cole-Parmer, Vernon Hills, IL, USA) is inserted into one side of a glass tube and is connected to the silver tubing. A few drops of NBS 22 oil are loaded into the glass tube with a thin tipped pipette. The open end of the glass tube is connected to the venting tube of a peristaltic pump. A low pressure is applied to transfer the viscous oil into the silver tubing. The end of the silver tubing is sealed by crimping. Silver tubing filled with NBS 22 can be transferred to the semi-automated silver-tubing pinch and seal device [11] to make tubes containing nearly identical amounts of NBS 22 oil.

The δ^2H measurements were performed with a TC/EA reduction unit (ThermoFinnigan, Bremen, Germany) equipped with a Costech Zero-Blank 50-position autosampler, a ConFlo IV gas introduction system (Thermo Fisher, Bremen, Germany), and a Delta+ XP isotope-ratio mass spectrometer (Thermo, Bremen, Germany). The samples in the TC/EA carousel were purged with helium for 5 min at 890 mL/min. The helium carrier gas (120 mL/min) is fed from the top, as originally supplied. The original 0.6-m ¼-inch 5-Å zeolite gas chromatography (GC) column was replaced by a 1.0-m ¼-inch 5-Å zeolite GC column to ensure good peak separation. For δ^2H analysis, the reactor temperature controller was set at 1430°C and the GC temperature was maintained at 85°C; the graphite crucible was removed to reduce the between-sample memory. The reactor is repacked every 250 samples. The $\delta^2H_{measured}$ values have been corrected for the H_3^+ contribution by the mass spectrometric data acquisition and control software. The H_3^+ contribution is determined daily before measurements are performed, and the average H_3^+ contribution is 2.75%. Once measurement results are obtained from the mass spectrometer, they are corrected for between-sample memory, for the effect of sample size on δ^2H value (so-called linearity correction), and drift with time of isotopic analysis. Uncertainties throughout this paper are one-sigma standard deviations unless otherwise specified.

RESULTS

Evaluation of drift and between-sample memory correction

The measurement results depend on the age and condition of the glassy carbon reactor of the TC/EA. The magnitudes of the correction for sample size on δ^2H value and of the drift correction are also correlated with the age of the glassy carbon. When the analyses were carried out with a freshly

Table 1. Typical analytical results from a portion of a day's run

Run no.	Description	Peak area/Vs	$10^3\ \delta^2H_{measured}$	$10^3\ k_{mem\_corr}$	$10^3\ \delta^2H_{mem\_corr}$	$10^3\ k_{lin\_corr}$	$10^3\ \delta^2H_{corrected}$
5	Antarctic water	103.4	−388.9			−0.9	−389.8
6	Antarctic water	95.2	−384.6			−5.5	−390.1
7	Antarctic water	102.1	−388.8			−1.6	−390.4
8	Antarctic water	104.1	−389.2			−0.5	−389.7
9	Antarctic water	102.4	−389.5			−1.4	−390.9
10	Antarctic water	102.1	−389.3			−1.6	−390.9
		101.5 ± 3.2	−388.4 ± 1.9				−390.3 ± 0.5
11	Tap water	113.5	−55.8	4.9	−50.9	1.4	−49.5
12	Tap water	109.2	−51.5	0	−51.5	0.7	−50.8
13	Tap water	94.6	−48.3	0	−48.3	−1.7	−50.0
14	Tap water	107.2	−51.1	0	−51.1	0.4	−50.7
15	Tap water	116.4	−52.2	0	−52.2	1.9	−50.3
16	Tap water	111.6	−51.4	0	−51.4	1.1	−50.3
		108.7 ± 7.6	−51.7 ± 2.4		−50.9 ± 1.3		−50.3 ± 0.5

k_{mem_corr} is between-sample memory correction; k_{lin_corr} is linearity correction; column 6 is column 4 + column 5; column 8 is column 4 + column 5 + column 7.

packed glassy carbon reactor, the linearity correction and drift correction were very low and therefore not needed. Isotopic normalization is made with a LIMS (Laboratory Information Management System) for Light Stable Isotopes.[18] The results presented in this paper have been corrected for between-sample memory, for the effect of sample size on δ^2H value, and for drift with time of isotopic analysis when these corrections are necessary. Because the hydrogen blank is below the detection level from silver tubes, no blank correction was applied to these data presented in this paper.

Analytical results from a portion of a typical single-day run are shown in Table 1. Antarctic water, which is depleted in ^{2}H, is shown in the first six positions of Table 1, and it is followed by six measurements of a local tap-water reference. The first analysis of the tap-water reference appears to be too negative ($10^3\ \delta^2H_{measured} = -55.8$) compared with the other analyses, apparently as a result of between-sample memory. The quantity k_{mem_corr} is the between-sample memory factor. This is given as 4.9‰ for run 11 in Table 1. This value is determined by the difference between the first analysis of tap water and the average of the subsequent five measurements of tap water, which is $(((-51.5‰) + (-48.3‰) + (-51.1‰) + (-52.2‰) + (-51.4‰))/5) - (-55.8‰) = +4.9‰$. If the areas of the two samples are the same, about 1.5% of a sample is contributed as memory to the following sample. The value of 1.5% is applicable only for this particular run, and it needs to be determined daily. Column 6 in Table 1, $\delta^2H_{mem\_corr}$, gives the memory-corrected δ^2H value. Comparing column 4 and column 6, one observes the improved uncertainty, from 2.4‰ to 1.3‰, obtained by correcting for between-sample memory Some users may prefer to ignore the first analysis of a new material, such as run 11, and this strategy is fully satisfactory. The measured δ^2H value is affected by the amount of sample (Figs. 1 and 2). This so-called linearity correction, k_{lin_corr}, is listed in column 7. This is calculated from the relationship between peak area and measured isotopic composition. A separate plot is determined for each material in this study (see Figs. 1 and 2). The linearity correction factors for each analysis in Table 1 are determined relative to the average peak area of the analyses of the material. Thus, an analysis having a peak area identical to the average peak area would have a correction of zero in the column labeled $10^3\ k_{lin\_corr}$. After the linearity correction is applied, there is a significant improvement in uncertainty, from 1.3‰ to 0.5‰ (Table 1). This data-evaluation protocol is used for all the measurement results presented in this paper.

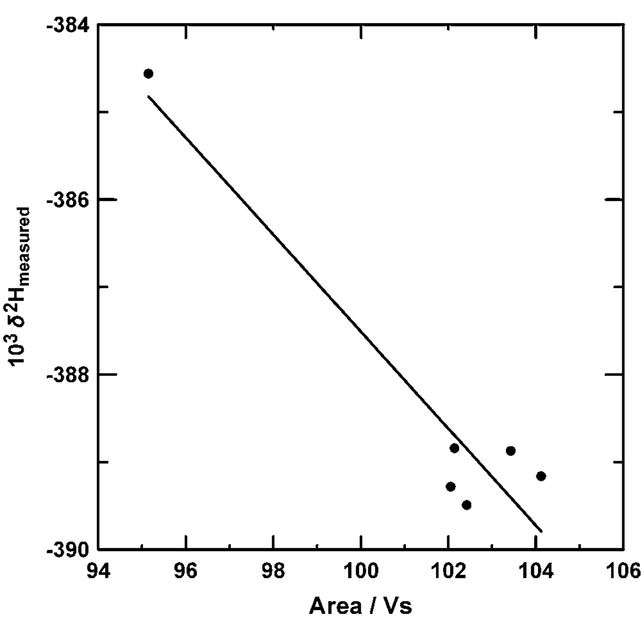

Figure 1. Hydrogen isotopic composition versus peak area of the Antarctic water sample (run numbers 5 through 10 in Table 1). The $\delta^2H_{measured}$ values have been corrected for H_3^+ contribution by the mass spectrometric data acquisition and control software and for between-sample memory. The linear fit equation is $10^3\ \delta^2H = -0.554 \times$ peak area $-$ 332.1. The average peak area used for determination of each linearity correction is 105 Vs.

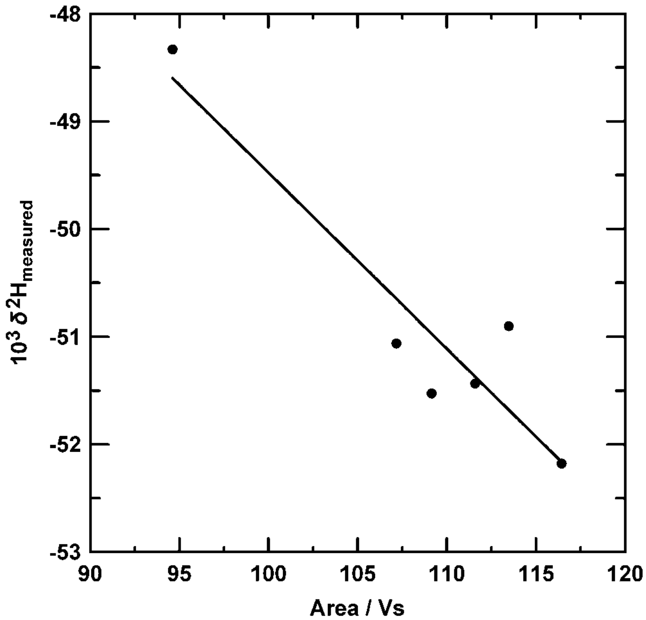

Figure 2. Hydrogen isotopic composition versus peak area of the tap water sample (run numbers 11 through 16 in Table 1). The $\delta^2H_{measured}$ values have been corrected for H_3^+ contribution by the mass spectrometric data acquisition and control software and for between-sample memory. The linear fit equation is $10^3\ \delta^2H = -0.1633 \times$ peak area $-$ 33.1. The average peak area used for determination of each linearity correction is 105 Vs.

Approach 1: Calibration with two waters having δ^2H values substantially different from that of NBS 22

In this approach, NBS 22 oil was analyzed in silver tubes and in silver capsules with aliquots of two isotopic reference waters. The typical sequence of samples and references used in this study is ten Antarctic isotopic reference waters ($\delta^2H_{VSMOW-SLAP} = -399.5‰$), six local tap-water isotopic references ($\delta^2H_{VSMOW-SLAP} = -62.3‰$), six NBS 22 oil samples, six local tap-water isotopic references, and six Antarctic isotopic reference waters. This populates 28

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Table 2. Hydrogen isotopic measurements of NBS 22 oil in this study using normalization with two reference waters differing substantially in isotopic composition

Date	Description	Amount or length of tube	Peak area/Vs	$10^3\ \delta^2H_{measured}$	$10^3\ \delta^2H_{VSMOW–SLAP}$
10/05/2009	Ag capsule	197 μg	101.8	−145.01	−115.30
10/05/2009	Ag capsule	167 μg	86.3	−143.88	−113.82
10/05/2009	Ag capsule	206 μg	109.3	−143.28	−112.95
10/05/2009	Ag capsule	194 μg	101.3	−144.87	−114.57
10/05/2009	Ag capsule	175 μg	91.2	−144.24	−113.65
			98.0 ± 9.2	−144.3 ± 0.7	−114.1 ± 0.9 (n = 5)
11/13/2009	Ag capsule	195 μg	109.3	−102.43	−115.55
11/13/2009	Ag capsule	202 μg	111.0	−102.68	−115.94
11/13/2009	Ag capsule	203 μg	113.5	−101.50	−114.89
11/13/2009	Ag capsule	191 μg	105.1	−102.36	−115.88
11/13/2009	Ag capsule	210 μg	117.3	−101.21	−114.86
11/13/2009	Ag capsule	171 μg	95.2	−101.35	−115.14
			108.4 ± 8.6	−101.9 ± 0.6	−115.4 ± 0.5 (n = 6)
11/17/2009	Ag capsule	200 μg	117.2	−102.00	−114.92
11/17/2009	Ag capsule	204 μg	116.1	−100.84	−113.87
11/17/2009	Ag capsule	200 μg	115.5	−101.93	−115.04
11/17/2009	Ag capsule	193 μg	111.7	−101.58	−114.79
11/17/2009	Ag capsule	184 μg	108.3	−101.54	−114.84
11/17/2009	Ag capsule	172 μg	100.3	−101.62	−115.00
			110.4 ± 6.5	−101.6 ± 0.4	−114.7 ± 0.4 (n = 6)
01/07/2010	Ag tube	2.5 mm	107.3	−112.32	−115.70
01/07/2010	Ag tube	2.5 mm	109.5	−112.34	−115.72
01/07/2010	Ag tube	2.5 mm	108.0	−112.97	−116.32
01/07/2010	Ag tube	2.5 mm	106.6	−111.62	−115.04
01/07/2010	Ag tube	2.5 mm	108.5	−112.92	−116.28
			108.0 ± 1.2	−112.4 ± 0.5	−115.8 ± 0.5 (n = 5)
01/12/2010	Ag tube	2.5 mm	108.3	−104.05	−116.54
01/12/2010	Ag tube	2.5 mm	108.3	−103.62	−116.09
01/12/2010	Ag tube	2.5 mm	108.3	−104.45	−116.94
01/12/2010	Ag tube	2.5 mm	108.3	−104.89	−117.38
01/12/2010	Ag tube	2.5 mm	108.3	−103.93	−116.39
			108.3 ± 0.03	−104.9 ± 0.5	−116.7 ± 0.5 (n = 5)
02/16/2010	Ag tube	2.5 mm	99.3	−103.6	−115.4
02/16/2010	Ag tube	2.5 mm	99.3	−103.1	−114.9
02/16/2010	Ag tube	2.5 mm	100.0	−104.6	−116.4
02/16/2010	Ag tube	2.5 mm	100.5	−103.8	−115.6
02/16/2010	Ag tube	2.5 mm	100.8	−104.3	−116.1
02/16/2010	Ag tube	2.5 mm	101.2	−103.6	−115.4
02/16/2010	Ag tube	2.5 mm	100.2 ± 0.8	−103.84 ± 0.5	−115.6 ± 0.6 (n = 6)
					−115.6 ± 0.8 (n = 28)*

* Average does not include the relatively poor results from 10/5/2009.
Measured δ^2H values were normalized with water references in silver tubes having $\delta^2H_{VSMOW–SLAP}$ values of −62.3‰ and −399.5‰. Averages and standard deviations are given in the last three columns.

positions in the TC/EA carousel. The first four analyses serve to condition the glassy carbon reactor and these δ^2H values are not used in calculations. A substantial advantage of the silver-tube technique is that one can make and load as many samples as desired at the beginning of a sequence to condition the analytical system, which leads to a remarkable improvement in reproducibility of the amount of sample (peak area) compared with the capsule method (Table 2).

The chromatograms from all water and oil samples have been carefully evaluated to confirm high-quality measurement results having no observable matrix effects. Figures 3 and 4 show typical chromatograms of water and oil, and these chromatograms show that the peak retention times, peak widths, and baselines are nearly identical, indicating that the conversion into gaseous hydrogen from either material is very similar and presumably quantitative, suggesting that the isotopic results are reliable. There is a concern that the release of nitrogen from nitrogen-bearing materials may affect the δ^2H measurements by as much as 20‰.[23] Because neither water nor NBS 22 oil contains nitrogen, there can be no nitrogen interference with these isotopic measurements.

On 10/05/2009, the TC/EA reactor was performing poorly as indicated by the high standard deviation of the $\delta^2H_{VSMOW–SLAP}$ value of 0.9‰ (Table 2). The measured δ^2H value is −144.3‰, which is about 27‰ different from the expected value. Nevertheless, normalizing with the isotopic reference waters sealed in silver tubes and interspersed among the NBS 22 samples yields a mean $\delta^2H_{VSMOW–SLAP}$ value of −114.1‰ on this day (day 1 of Fig. 5). The benefit of normalization is that this mean value of −114.1‰ differs from other measurements by less than 2‰ although the δ^2H value before normalization differs by 27‰ from other unnormalized values. The measurement results from 10/05/

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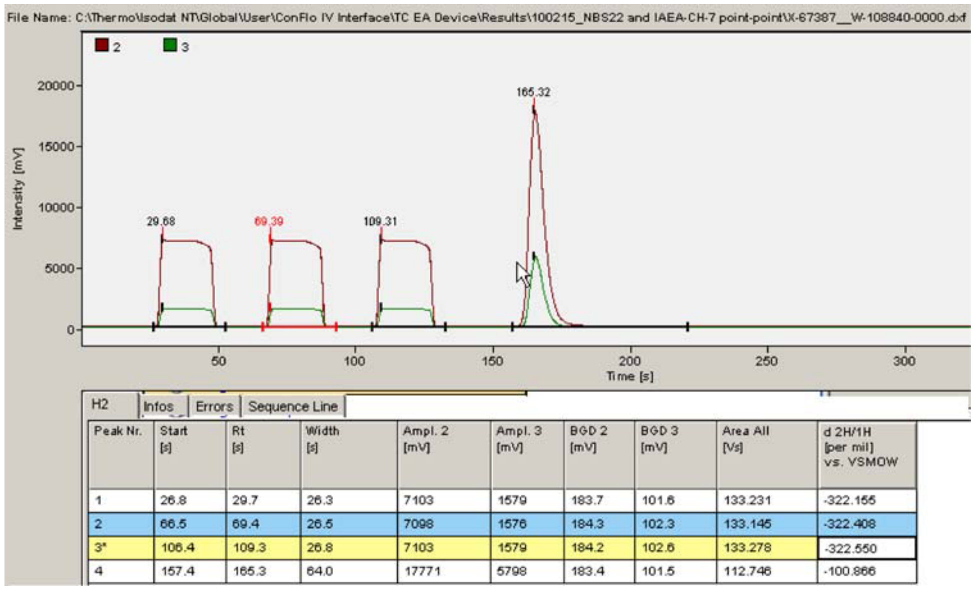

Figure 3. Typical chromatogram of the analysis of water.

2009 are presented for illustration only, and were not used in calculating the δ^2H value of NBS 22 oil. The normalized $\delta^2H_{VSMOW-SLAP}$ values for NBS 22 obtained from silver capsules or from silver tubes are identical within analytical uncertainty. However, the average reproducibility of the peak areas with the silver tubes is better than 1%, which is about an order of magnitude better than that measured with silver capsules (Table 2). A mean $\delta^2H_{VSMOW-SLAP}$ value of -115.6 ± 0.8‰ (1 σ and n = 28) is determined by using silver tubes and using silver capsules to introduce the NBS 22 oil into the TC/EA system (Table 2). The two reference waters used for calibration in Table 2 differ substantially in isotopic composition, for which the between-sample memory correction and scale correction can be substantial.

Approach 2: Calibration with two waters having δ^2H values closer to that of NBS 22

To minimize between-sample memory correction and scale correction, and to improve the measurement accuracy, two isotopic reference waters are used that are nearer in isotopic composition to that of the unknown to be calibrated. In Table 3 reference waters with $\delta^2H_{VSMOW-SLAP}$ values of -62.3 and -150.7‰ are used for calibration. A $\delta^2H_{VSMOW-SLAP}$ value of -117.2 ± 0.4‰ (n = 13) is determined for NBS 22 oil. An improvement in the uncertainty may be the result of using isotopic reference waters with isotopic compositions nearer that of the unknown, presumably because between-sample memory correction and scale correction are lower than in approach 1.

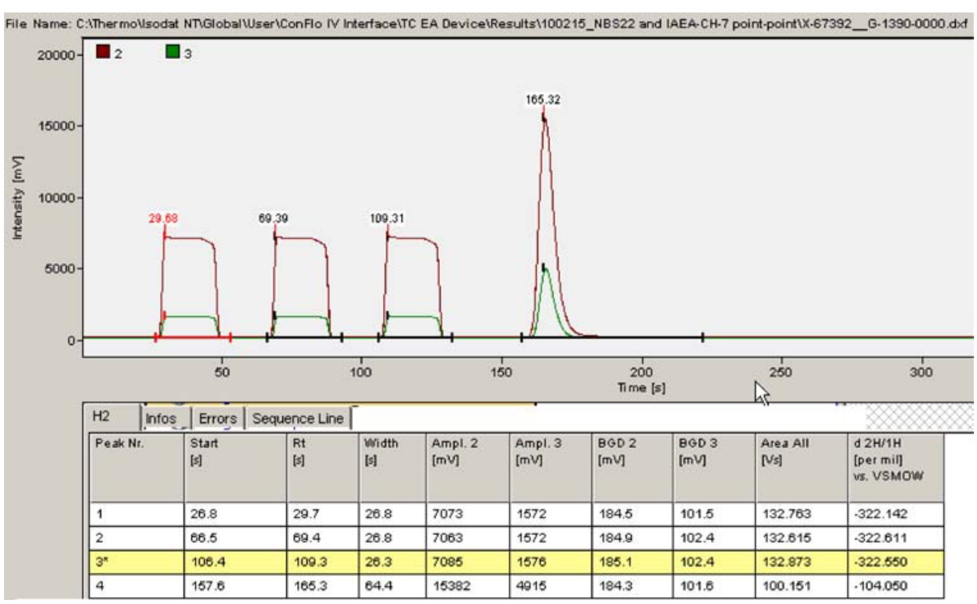

Figure 4. Typical chromatogram of the analysis of NBS 22 oil.

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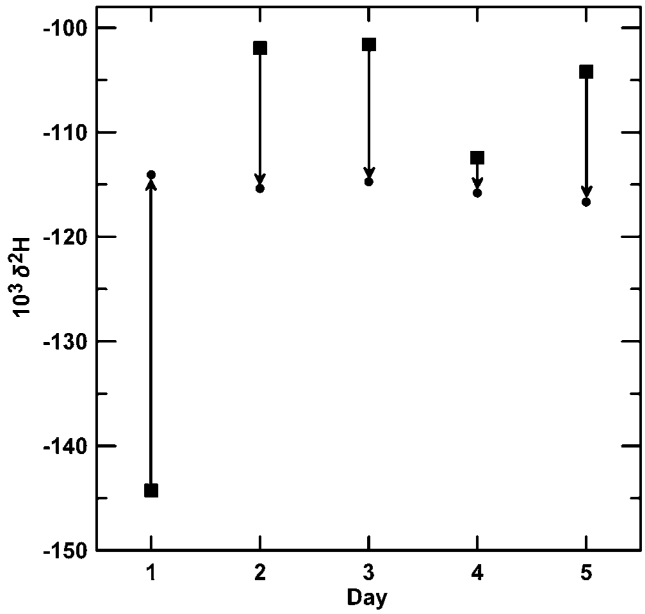

Figure 5. Effect of normalization on isotopic data. Day 1 is 10/05/2009; day 2 is 11/13/2009; day 3 is 11/17/2009; day 4 is 1/7/2010; day 5 is 1/12/2010. On day 1, the TC/EA reactor was performing poorly; nevertheless, the measured mean δ^2H value of −144.3‰ was normalized with aliquots of the two isotopic reference waters to a $\delta^2H_{VSMOW-SLAP}$ value of −114.1‰, showing the benefits of normalization.

Approach 3: Calibration with a single water almost identical in δ^2H value to that of NBS 22

Taking approach 2 to a higher level yields a point-to-point calibration in which a single reference water is used for calibration, and its $\delta^2H_{VSMOW-SLAP}$ value is selected to be as close as possible to that of the material to be calibrated. This method yields a $\delta^2H_{VSMOW-SLAP}$ value of -116.7 ± 0.5‰ (n = 18), as shown in Table 4. In this approach, between-sample memory correction and scale correction are virtually eliminated.

DISCUSSION

Among these three approaches for NBS 22 calibration, in principle the point-to-point method should yield most reliable values because the between-sample memory correction and scale correction are lowest. We could take only the $\delta^2H_{VSMOW-SLAP}$ value of -116.7 ± 0.5‰ obtained from the point-to-point approach as the final new value for NBS 22. However, the $\delta^2H_{VSMOW-SLAP}$ value of -117.2 ± 0.4‰ calibrated from reference waters with $\delta^2H_{VSMOW-SLAP}$ values of −62.3 and −150.7‰ is identical within analytical uncertainty to the value from the point-to-point method within analytical uncertainty. Thus, the final $\delta^2H_{VSMOW-SLAP}$ value of -116.9 ± 0.5‰ (n = 31) for NBS 22, an average of the results from Tables 3 and 4, is selected as the most reliable value, and the uncertainty is increased from 0.5‰ to 0.8‰ to account for uncertainty in the laboratory reference waters, yielding a value of -116.9 ± 0.8‰. The value of -115.6 ± 0.8‰ determined in approach 1 is about 1.3‰ more positive that the final calculated value of −116.9‰. Considering the potential problems associated with the between-sample memory correction and the larger scale correction, these measured values were excluded in the calculation of the final value.

From a comparison of the measurement results of the three approaches, we conclude that the point-to-point method yields the value with the lowest uncertainty for calibration of a single reference material. This method virtually eliminates the between-sample memory correction and scale correction. However, for analyzing unknown samples, the point-to-point approach (approach 3) cannot be used, and either approach 1 or 2 is needed. It is suggested that the water references used should have δ^2H values that span the range of expected δ^2H values of the unknowns; however, the range should not be larger than necessary to minimize the uncertainty contributed by between-sample memory and a scale correction in a TC/EA system.

Table 3. Hydrogen isotopic measurements of NBS 22 oil in this study using normalization with two reference waters differing minimally in isotopic composition

Date	Description	Amount or length of tube	Peak area/Vs	$10^3\ \delta^2H_{measured}$	$10^3\ \delta^2H_{VSMOW-SLAP}$
2/23/2010	Ag tube	2.5 mm	102.1	−104.9	−116.9
2/23/2010	Ag tube	2.5 mm	100.8	−104.5	−116.5
2/23/2010	Ag tube	2.5 mm	101.0	−104.8	−116.8
2/23/2010	Ag tube	2.5 mm	101.2	−105.5	−117.5
2/23/2010	Ag tube	2.5 mm	101.4	−104.8	−116.8
2/23/2010	Ag tube	2.5 mm	102.2	−105.2	−117.3
			101.5 ± 0.6	−105.0 ± 0.3	−117.0 ± 0.4
2/23/2010	Ag tube	2.5 mm	103.6	−104.6	−117.2
2/23/2010	Ag tube	2.5 mm	103.6	−104.5	−117.2
2/23/2010	Ag tube	2.5 mm	103.8	−104.7	−117.4
2/23/2010	Ag tube	2.5 mm	103.9	−105.0	−117.7
2/23/2010	Ag tube	2.5 mm	102.7	−104.7	−117.4
2/23/2010	Ag tube	2.5 mm	103.5	−104.7	−117.9
2/23/2010	Ag tube	2.5 mm	103.6	−105.2	−116.8
			103.6 ± 0.4	−104.7 ± 0.3	−117.4 ± 0.4
					−117.2 ± 0.4 (n = 13)

Measured δ^2H values were normalized with water references in silver tubes having $\delta^2H_{VSMOW-SLAP}$ values of −62.3‰ and −150.7‰. Averages and standard deviations are given in the last three columns.

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Table 4. Hydrogen isotopic measurements of NBS 22 oil in this study using point-to-point normalization

Date	Description	Amount or length tube	Peak area/Vs	$10^3\ \delta^2H_{measured}$	$10^3\ \delta^2H_{VSMOW-SLAP}$
2/12/2010	Ag tube	2.5 mm	103.0	−95.0	−117.1
2/12/2010	Ag tube	2.5 mm	102.5	−94.9	−116.9
2/12/2010	Ag tube	2.5 mm	103.2	−94.7	−116.7
2/12/2010	Ag tube	2.5 mm	103.2	−94.9	−116.9
2/12/2010	Ag tube	2.5 mm	102.1	−94.8	−116.9
2/12/2010	Ag tube	2.5 mm	103.6	−95.0	−117.1
			102.9 ± 0.5	−94.9 ± 0.1	−116.9 ± 0.1
2/15/2010	Ag tube	2.5 mm	99.3	−104.2	−117.6
2/15/2010	Ag tube	2.5 mm	98.3	−103.8	−117.1
2/15/2010	Ag tube	2.5 mm	98.5	−103.2	−116.5
2/15/2010	Ag tube	2.5 mm	100.2	−103.5	−116.8
2/15/2010	Ag tube	2.5 mm	99.5	−103.7	−117.0
2/15/2010	Ag tube	2.5 mm	98.9	−103.9	−117.2
			99.1 ± 0.7	−103.7 ± 0.4	−117.0 ± 0.4
2/18/2010	Ag tube	2.5 mm	100.1	−103.2	−115.7
2/18/2010	Ag tube	2.5 mm	99.8	−103.2	−115.7
2/18/2010	Ag tube	2.5 mm	101.0	−104.3	−116.8
2/18/2010	Ag tube	2.5 mm	99.5	−103.5	−116.0
2/18/2010	Ag tube	2.5 mm	99.5	−104.1	−116.6
2/18/2010	Ag tube	2.5 mm	100.0	−104.3	−116.8
			100.0 ± 0.6	−103.8 ± 0.5	−116.3 ± 0.5
					−116.7 ± 0.5 (n = 18)

Measured δ^2H values were normalized with a single reference water in silver tubes with a $\delta^2H_{VSMOW-SLAP}$ value of −115.3‰. Averages and standard deviations are given in the last three columns.

Table 5. Selected δ^2H published measurements of NBS 22 oil

Name and Laboratory	$\delta^2H_{VSMOW-SLAP}$ (‰)	Reference
M. Coleman, BP Research Centre, Sunbury-on-Thames, UK	−115.2	12
W. G. Mook, Isotope Physics Laboratory, University of Groningen, The Netherlands	−120.4	12
J. R. O'Neil, U.S. Geological Survey, Menlo Park, CA, USA	−119.8	12

Selected previous δ^2H measurements of NBS 22 oil are tabulated in Table 5 and date from the 1980s. No analytical methods were provided by Ref. 12. The new $\delta^2H_{VSMOW-SLAP}$ value of NBS oil of −116.9 ± 0.8‰ described in this paper is close to the value of −115.2‰ measured by M. Coleman in the 1980s. This analytical work shows that the silver-tube method is useful for isotopic analysis of both water and oil.

CONCLUSIONS

The silver-tube method is useful for isotopic analysis of both water and oil. Using this method, a new $\delta^2H_{VSMOW-SLAP}$ value of NBS oil of −116.9 ± 0.8‰ (1σ and n = 31) has been determined. The new value agrees well with previous measurements, and the reproducibilities of sample amount and isotopic composition of this new method suggest its reliability.

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